Reaction of 2-Aryl-azirines with Rhodium(1) Complexes

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Chlorodicarbonylrhodium(I) dimer, [Rh(CO)₂-Cl]₂, or chlorocarbonylbis(triphenylphosphine)rhodium, [(Ph₃P)₂Rh(CO)Cl], reacts with 2-aryl-azirines under gentle conditions (benzene, room temperature) to afford 2-styryl-indoles.

A RECENT publication has described the Group 6 metal carbonyl-induced dimerization of azirines to pyrazines and dihydropyrazines under gentle conditions.1 We now report that rhodium(I) carbonyl complexes effect a different, interesting, and useful reaction with 2-aryl-azirines.

Reaction of 2-aryl-azirine (1; R = H, Me, OMe, or Br) with chlorodicarbonylrhodium(I) dimer (2) or chlorocarbonylbis(triphenylphosphine)rhodium [(2) is superior for work-up purposes] in benzene at room temperature for 24 h affords 2-(2-arylvinyl)-indoles (3) in 39-80% yields based on (2) (3; R = H, 57%; R = Me, 80%, m.p. 213—214 °C; R = OMe, 76%, m.p. 233-235 °C; R = Br, 39%, m.p. 242-244 °C). The structures of the products were determined on the basis of analytical and spectral data (3, R = H, is a known compound²). 2-Arylethylene indoles are important intermediates in alkaloid synthesis.2,3

The reagent concentrations have a significant influence on the reaction. Using a 10:1 mole ratio of azirine to

rhodium carbonyl gave the indole as the only product (e.g., 3, R = Me). Increasing the proportion of rhodium carbonyl to give a 6-7:1 ratio of (1):(2) affords (3) and a trace amount of 2,5-diarylpyrrole.4 Use of a 2:1 mole ratio of (1): (2) gave the 2,5-diarylpyrrole as the principal product, with (3) and an unidentified rhodium complex as by-products.

$$p - RH_4C_6 \xrightarrow{N} + [Rh(CO)_2CI]_2 \xrightarrow{Room \ temp} R \xrightarrow{N} C_6H_4R-p$$
(3)

The following general procedure was used. To 1 mmol of (2) in 50 ml of anhydrous benzene was added 7 mmol of (1) in 25 ml of benzene. The reaction mixture was stirred at room temperature for 24 h and filtered. The precipitate was washed with benzene (50 ml) and the washings were added to the filtrate. The filtrate was concentrated in vacuo and the indole was purified by chromatography on Florisil.

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